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Structural aspects of the threefold surface of icosahedral Al–Pd–Mn

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Abstract

We report the first STM study of a threefold surface of an icosahedral quasicrystal. We find that a rough, cluster-dominated structure evolves into a terrace-step morphology, with increasing temperature. The terraces display a fine structure whose long-range order is consistent with threefold symmetry. The fine structure includes small, deep holes. The steps can be very straight, serving to bound equilateral triangles (or portions thereof). These straight steps can cut directly across meandering step edges, superimposing a triangular 'shadow' upon the other terrace-step landscape. The data suggest that the triangles grow outward from a special type of central point. The triangles may represent the initial stages of facetting. © 2000 Elsevier Science B.V. All rights reserved.

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Quasicrystals are well-ordered, but aperiodic, intermetallics. They typically exhibit a rotational symmetry which is crystallographically forbidden. It is of interest to determine whether, and in what ways, their surfaces resemble their bulk. On the one hand, this issue is motivated by practical interest – a desire to understand the origins of their low friction and reduced adhesion. On the other hand, this issue is motivated by fundamental curiosity – a desire to understand whether the forces which stabilize a three-dimensional structure remain in effect at its two-dimensional truncation.

Many experimental techniques can probe surface structure. For a material as complex as a quasicrystal, most techniques will provide only a partial answer, and a complete picture will evolve only after many different types of experiments. In this paper, we apply one technique, scanning tunneling microscopy (STM). This technique can provide information both about local and long-range structure. For quasicrystalline surfaces, however, it has not yet provided atomic-scale resolution nor chemical speciation.

Surfaces of quasicrystals can be prepared in a

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variety of ways. The most common, sputtering and annealing, can yield terrace-step features when the surfaces have compositions close to that of the bulk. (Cleavage can produce much rougher surfaces [1].) Scanning tunneling microscopy studies of the terrace-step-type surfaces have thus far been reported only for fivefold surfaces of icosahedral materials [2–9] and tenfold surfaces of decagonal materials [9–12]. These studies have often revealed small local structures, e.g., pentagons, which are consistent with the symmetry of the zone axis perpendicular to the surface. In some cases, the STM has even revealed a longer-range order on the terraces, again consistent with the symmetry expected for the bulk termination.

However, quasicrystals also possess other high-order symmetry axes, and surfaces perpendicular to these axes have not yet been studied with STM, perhaps because they are less exotic than the crystallographically forbidden fivefold and tenfold symmetries. Nonetheless, they are essential to build a complete database of information on quasicrystalline surfaces. In this paper, we report an STM study of the threefold surface of icosahedral Al–Pd–Mn. While this surface has not been studied previously with STM, it has been studied with low-energy electron diffraction (LEED) [13–15]. The latter technique has shown that a quasicrystalline(-like) surface can be prepared, after sputtering, by prolonged annealing in the range 650–850 K. At lower annealing temperatures, a cubic (111) overlayer develops. At even lower temperatures, an unidentified crystalline phase develops [14]. However, the crystalline phases are not the focus of the present work. Instead we concentrate on the temperature regime which produces the quasicrystalline(-like) LEED pattern.

The experiments were performed with equipment, and under conditions, similar to those described previously in a study of the fivefold surface [5]. The tunneling voltage was 1.0 V, and the current was 0.3–0.6 nA. Use of lower tunneling currents, down to 0.03 nA, did not produce a qualitative difference in the images.

Two different samples were used. Each of these samples went through two cycles of being polished and then examined with STM. Hence, in total, the experiments were performed on four different surfaces. After any given annealing temperature, a variety of structures could be found on the surface, based upon examination of many images at different surface areas, over all four of these surfaces. In other words, the surfaces are heterogeneous. However, it is our strong impression that the surfaces generally evolve according to the sequence described below, even though different regions may not change exactly in parallel. The sample was typically annealed at the stated temperature for 0.5–4 h, then cooled to 300 K for imaging. A threefold LEED pattern was observed in parallel with the STM measurements. The LEED optics were too poor, however, to resolve significant structure in the pattern.

Fig. 1 shows two examples of rough surfaces obtained at the lowest annealing temperatures (800–850 K). Fig. 1a and c are micrographs, while Fig. 1b and d are corresponding line scans. Both surfaces have cluster-like structures, the clusters being about 10 nm in diameter. However, the clusters are better separated in Fig. 1a than in Fig. 1c, which leads to higher roughness in the former case. This is illustrated by the line scans, Fig. 1b and d. The values of the root mean square roughness are 2.3 and 0.96 nm, respectively. (Corresponding arithmetic means are 1.9 and 0.77.) These clusters may represent the cubic structure, although they may also (by analogy with suggestions for the fivefold surface [8,16]) represent a quasicrystalline intermediate between the rough cubic phase and the quasicrystalline terrace-step structure. We note that in this temperature range, the LEED pattern is already that of the quasicrystalline(-like) surface [14,15].

At slightly higher temperatures, or longer annealing times, the clusters become more isolated and terraces emerge. Both features can co-exist. This is illustrated in Fig. 2. Images are poor for such surfaces because the remaining clusters tend to streak and change the tip characteristics during the scan. The step edges are rough and meandering, and may be pinned by clusters.

Around 875–900 K, the clusters disappear. The step edges are still very rough. This is shown by the large-scale image of Fig. 3a. The terraces exhibit a fine structure, which is shown in Fig. 3b.

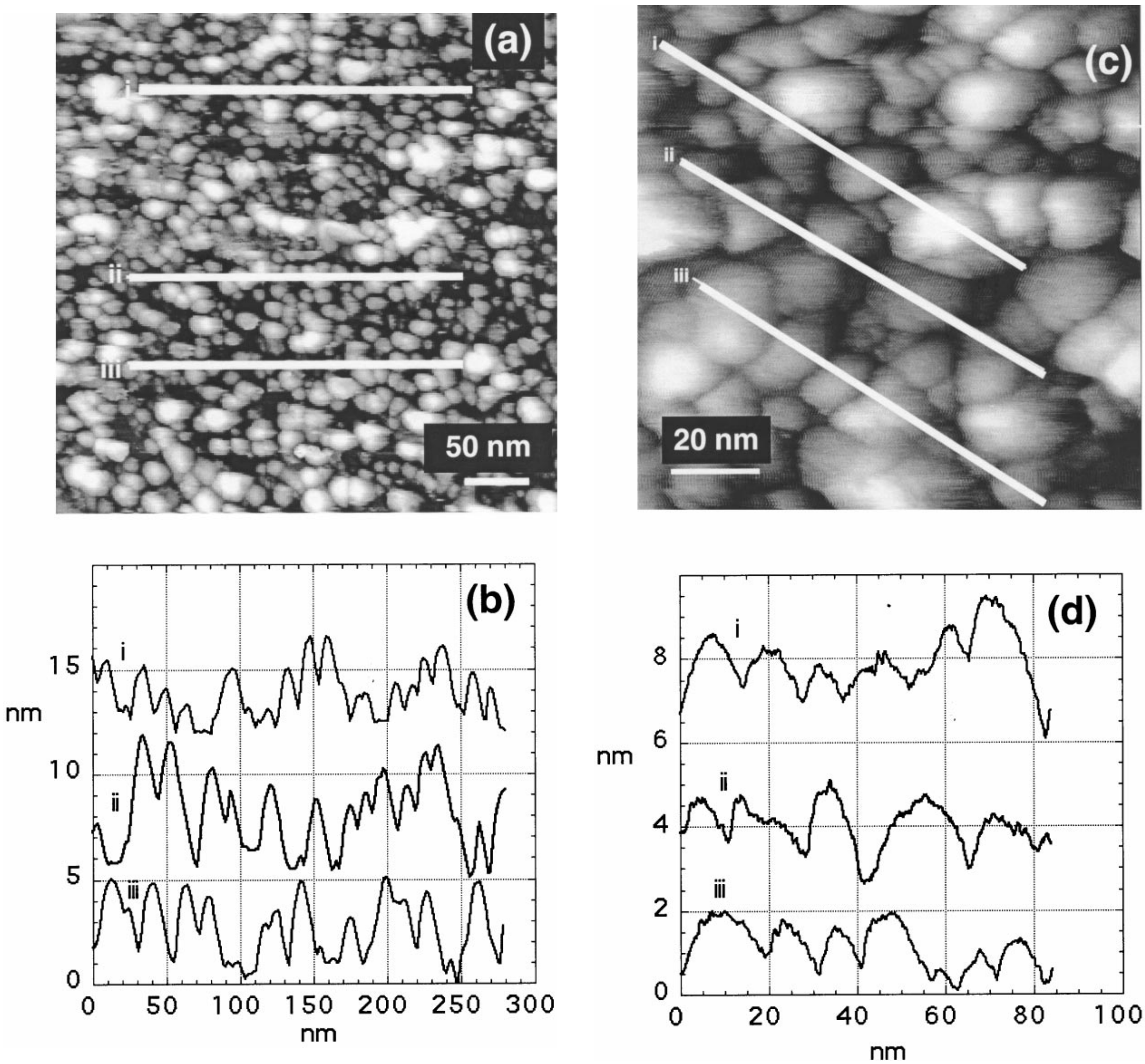

Fig. 1. Two examples of cluster-dominated surface structure. (a) STM image, obtained after annealing at 850 K for 1 h; total area, 400 nm × 400 nm. (b) Line scans corresponding to (a). (c) STM image, obtained after annealing at 800 K for 1 h; total area, 100 nm × 100 nm. (d) Line scans corresponding to (c).

The fine structure appears random upon visual inspection. The most pronounced features are small holes, which appear black in Fig. 3b. The line scans (Fig. 3c) reveal that these holes are about 0.2 nm deep, while the rest of the surface has a peak-to-peak corrugation of about 0.1 nm. (The root mean square roughness is 0.06 nm and the arithmetic mean is 0.04 nm.) The holes are about 1–2 nm wide. It should be noted that STM images the electronic density contours, which may or may not reflect nuclear positions. Hence, the 'corrugation' and 'holes' on the terraces may not reflect directly the atomic topography.

When Fig. 3b is corrected for distortion, its

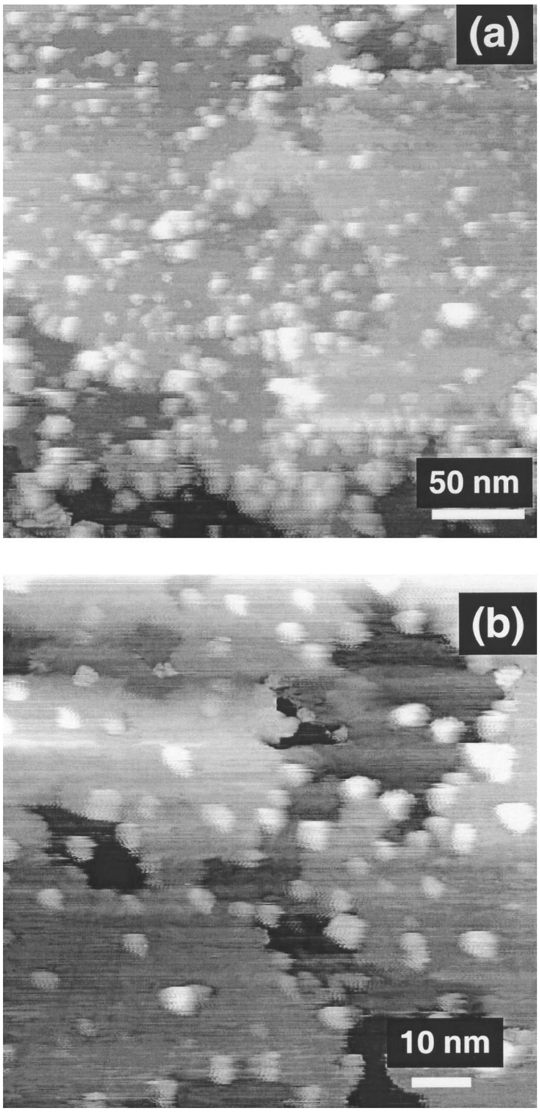

Fig. 2. Two examples of coexisting cluster and terrace-step structures. (a) STM image, obtained after annealing at 800 K for 4 h; total area, 300 nm × 300 nm. (b) STM image, obtained after annealing at 800 K for 2 h; total area, 90 nm × 90 nm.

Fourier transform exhibits sixfold symmetry, hence indicating a degree of order in the real-space structure. The sixfold autocorrelation function of Fig. 3d confirms this. Note that both the Fourier transform and the autocorrelation introduce an inversion center, so that a threefold structure in real-space becomes sixfold after each manipulation. Hence, both manipulations are consistent with the observation of a threefold pattern in LEED under similar conditions [15].

At 900 K, straight step edges emerge. They usually coexist with the meandering step edges. The straight step edges are the boundaries of equilateral triangles, or portions of such triangles. The straight step edges can actually cut across the meandering step edges. This produces an image such as Fig. 4a, where the triangle looks like a shadow cast upon the underlying landscape. This intriguing type of structure is illustrated also in Fig. 4b. Smaller triangles are illustrated in Fig. 4c. The triangles can be either depressions in, or protrusions from, the surface. The large triangles in Fig. 4a and b are depressions.

As shown in Fig. 4a and b, one often finds several triangles – or sections of triangles – nested concentrically. The straight step edges are always parallel, no matter how large the scale of the image. This is especially striking in Fig. 4c, where three non-overlapping triangles are shown, all with parallel step edges. Furthermore, only three step orientations are ever observed. Hence, the orientations of the straight steps must be controlled by the fundamental threefold symmetry of the zone axis. This is consistent with the relative orientation of the triangles in STM, and the LEED pattern observed in parallel experiments (in the same chamber).

Higher temperatures were not accessible because of phase decomposition of the sample.

We can speculate about the mechanism and driving force for evolution of the straight step edges. The fact that they form closed triangles, and even concentric triangles, rather than randomly intersecting lines, suggests strongly that they grow outward from a point of origin which is somehow unique. One can imagine that the small triangles in Fig. 4c could be the precursors to the larger ones in Fig. 4a and b. The small triangles might grow larger with more severe annealing, one of the triangles eventually overtaking and consuming the others. The small triangles do seem to have something at their centers, as can be seen in Fig. 4c. At this time, however, we cannot determine the nature of the centers of the small

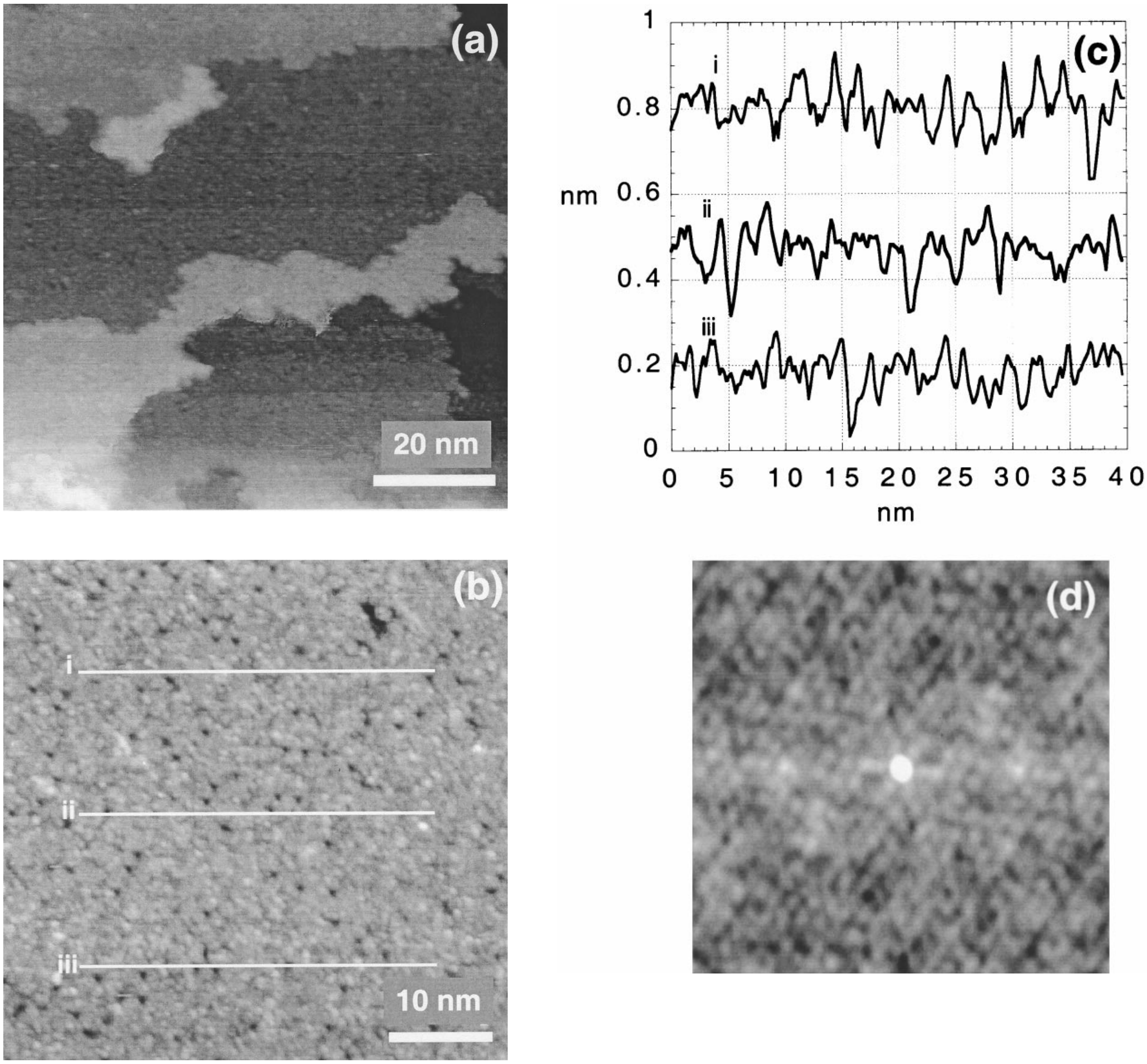

Fig. 3. Terrace-step structure with meandering steps only. (a) STM image, obtained after annealing at 900 K for 0.5 h; total area, 80 nm × 80 nm. (b) STM image of the terrace fine structure, obtained after annealing at 875 K for 2 h; total area, 50 nm × 50 nm. (c) Line scans corresponding to (b). (d) Autocorrelation transform of (b).

triangles. It may be that the triangles are the first stages of facetting, with their straight edges perpendicular to the three fivefold axes. In a previous study, we have shown that the threefold surface does tend to facet, toward the fivefold axes and toward an unidentified direction [15].

There are some indications that the triangles are related to the black holes. The density of the holes seems to increase between 800 and 900 K. At a temperature slightly lower than 900 K, just before triangles appear, we found at different places a density of holes so high that they seem to outline the edges of triangles. Thus, we speculate that the holes may be the precursors to the small

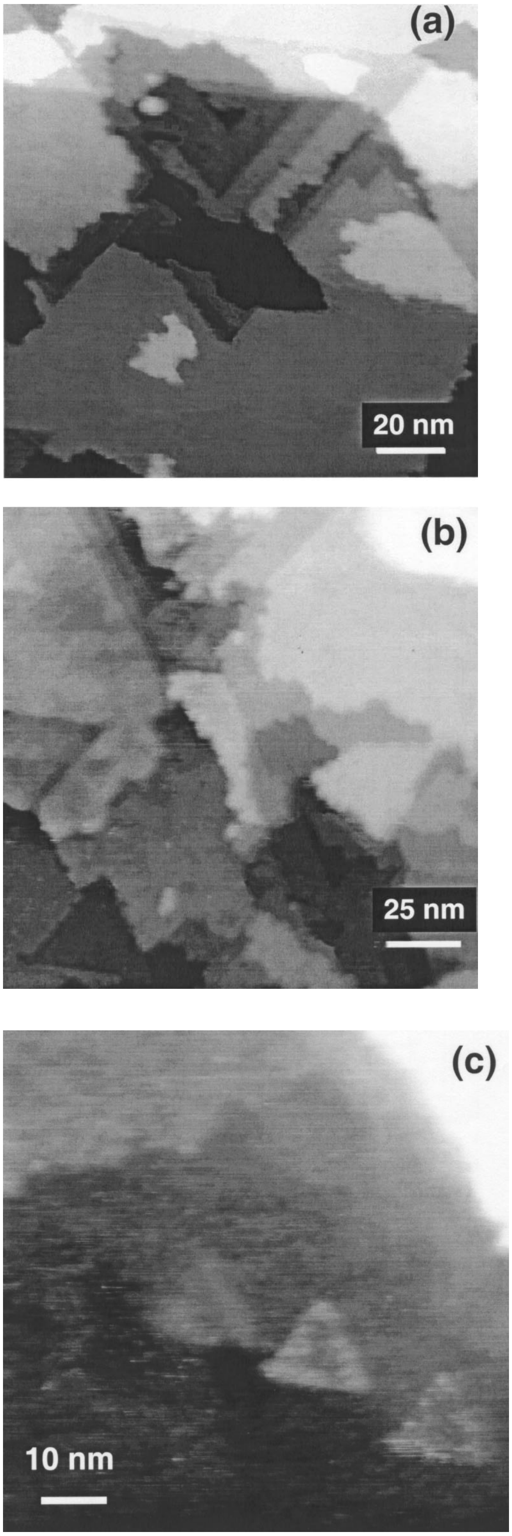

Fig. 4. Three examples of terrace-step structures, where meandering and straight step edges coexist. All images obtained after annealing at 900 K for 0.75 h. (a) Total area, 140 nm × 140 nm. (b) Total area, 150 nm × 150 nm. (c) Total area, 60 nm × 60 nm.

triangles, and the small triangles in turn may be the precursors to the larger ones.

It is interesting to compare these observations with those for the fivefold surface, prepared under similar conditions. There, a progression was also observed, from a rough, cluster-dominated structure to a terrace-step structure, with increasing temperature. However, the step edges in the terrace-step structure were always rough (meandering); no straight step edges were ever observed. For the fivefold surface, a fine structure was also observed on the steps, with a clear rotational symmetry and long-range order, as revealed by the Fourier transform and autocorrelation function. However, the peak-to-peak corrugation was about 0.08 nm; the small deep holes were not observed. Hence, the threefold surface differs from the fivefold, for comparable conditions of preparation, in two main ways: First, it develops straight step edges, which encompass equilateral triangles; and second, it exhibits 0.2 nm deep depressions in the terrace fine structure, which are deeper than depressions observed on the fivefold surface, under comparable tunneling conditions.

In summary, this STM study of the threefold surface of icosahedral Al–Pd–Mn has shown the same general trend of morphological development as for the fivefold surface: a rough, cluster-dominated structure evolves into a terrace-step configuration. The terraces display a fine structure whose long-range order is consistent with threefold symmetry. However, the fine structure on the terraces is rougher than on the fivefold surface, exhibiting holes that are 0.2 nm deep. Furthermore, the steps can be very straight, serving to bound equilateral triangles (or portions thereof) whose edges are always parallel. These straight steps can superimpose upon the meandering steps. The data suggest that the triangles grow outward from a special central point. These intriguing observations provoke further study.

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